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A Study of Aluminum Phosphates using Infrared Spectroscopy

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A STUDY OF ALUMINUM PHOSPHATES USING INFRARED SPECTROSCOPY

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A thesis presented to the Department of Chemistry of Union College in partial fulfillment of the requirements for the degree of Bachelor of Science with a Major in Chemistry.

By Michael Miller

Approved by H E Shaffer

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Abstract

The infrared spectra of aluminum metaphosphate, aluminum pyrophosphate, and the ortho acid phosphates were studied in the 2u to 15u region. The distinct absorption regions of each compound were located. The type of bond which caused the absorption is suggested. The spectra of the aluminum phosphates were found to be very similar to the spectra of other phosphates. The effect of heating the various aluminum phosphates to 600°C was investigated. A partial conversion of $Al(H_2PO_4)_3$ to $Al(PO_3)_3$ of $AlPO_4$ to $Al_4(P_2O_7)_3$ and $Al_4(P_2O_7)_3$ to $Al(PO_3)_3$ were observed.

The investigation of the aluminum phosphates was used as background for a determination of the nature of the alumina-aluminum phosphate catalyst used in the alkylation of phenol and to interpret the changes which take place upon the activation of the catalyst by heating for eight hours at 600°C. The inactivated catalyst was found to be alumina and aluminum orthophosphate. The activated catalyst was found to be alumina and aluminum pyrophosphate aluminum metaphosphate. The NH_4^+ ion which had been adsorbed by the catalyst during its preparation was found to desorb.

Historical and Theoretical Review:

The infrared investigation of the aluminum phosphate compounds is undertaken to establish a foundation for an infrared study of an alumina-aluminum phosphate catalyst. This catalyst has been used by workers at Union College(10) for the alkylation of phenol with numerous alcohols. A more complete knowledge of the composition of this catalyst and its function would be helpful in establishing a mechanism for the alkylation reaction.

There is a great deal of interest in the infrared spectra of inorganic salts at present. Numerous papers are being published containing inorganic spectra and new techniques of examining the spectra. A paper by Hunt, Wisherd and Bonham(5) contains the spectra of 64 naturally occuring minerals and their related compounds. Hunt and associates obtained particles in the range of 3u in size by sedimenting a fine powder dispersed in a column of water for three hours and then by removing the top portion of the solution and evaporating the water.(5) The spectra of 159 pure inorganic compounds are presented and analyzed in a paper by Miller, Veil and Wilkins.(9) Representative wave lengths for the absorption of many polyatomic ions are suggested. Miller and associates examine the samples as dry powders or Nujol mulls on salt blocks.(9) The spectra of 153 salts of the phosphorus oxy-acids are examined as dry powders or Nujol mulls on salt blocks in two papers by Corbridge and Lowe, and correlations between absorption

bands and molecular structure are suggested.(1) (2)

Aside from a spectrum of aluminum tetrametaphosphate in the first paper of Corbridge and Lowe,(1) there is no study of the infrared absorptions of aluminum phosphates in the literature. It, therefore, seems worthwhile to see if aluminum metaphosphate, aluminum pyrophosphate and the ortho acid phosphates of aluminum give good spectra, if the anions possess absorptions which are sufficiently characteristic for ananlytical purposes, and if the spectra are similar to the spectra of other phosphate compounds.

A discussion of the theory of infrared spectroscopy and of the various types of crystal and molecular vibrations that are caused by absorption in the infrared region of the electromagnetic energy spectrum is appropriate at this time. The absorption of infrared rays, by wavelengths 2u--30u, causes the atoms within a molecular structure to vibrate. The wavelength at which a molecule absorbs is a measure of the amount of electromagnetic energy it removes from the incenent beam of energy. The frequencies of absorptions depend upon the masses of the atoms, the strength of the binding forces and the configuration of the molecules and crystals. The binding forces have the strongest influence on the wavelength of energy absorbed. The stronger the bond the higher the frequency and the lower the wavelength of electromagnetic energy absorbed.

In a crystal composed of solely monatomic ions,

such as sodium chloride, potassium bromide, and calcium flouride only ionic lattice vibrations occur, in which the individual ions undergo translatory vibrations. The absorption is usually in the far ifrared region, 25-300u. If the compound is hydrated absorption peaks for water are present. Crystals containing polyatomic ions, such as metaphosphate, ammonium, and sulfate, have ionic lattice vibrations and internal molecular vibrations, which are due to the high energy vibrations of the covalent bonded atoms of the polyatomic ions. The ionic lattice vibrations cause shifts in the location of the absorption bands of the internal molecular vibrations which appear in the near infrared region 2-25u. In molecular solids, such as phosphorus and boric acid, the units are uncharged molecules held in the crystal lattice by weak Van der Waals forces and hydrogen bonding. The vibration of these bonds adsorbs energy in the far infrared region, and also cause shifts in the location of the absorption bands of the internal molecular vibrations of the polyatomic ions present. There are covalent solids, such as diamond quartz and silica, in which the lattice bonds are covalent. Both the lattice and internal molecular vibrations absorb in the near infrared region.(9)

Infared spectroscopy can be used to study adsorption and chemisorption on the surface of a solid. "Surface groups are differential from internal groups by the behavior of absorption bands as molecules are physically adsorbed. An atom or molecule physically adsorbed near

a surface group disturbs motions of atoms of the group, causing a shift in some group vibration frequencies. The magnitude of the shift indicates the strength of the interaction between the adsorbed molecules and the surface groups. The magnitude of the shift also depends on the geometric arrangement of the surface group and the adsorbed molecule. Chemical reactions between the adsorbed molecules and the surface groups are indicated by new bands." (7)

The complete infrared spectrum of a compound is highly characteristic. Any given functional group in a molecule absorbs at characteristic frequencies, which allow the researcher to fix the proper functional groups to a molecule. The absorption frequencies can be determined approximately by analysis of many different compounds containing the same functional group. The frequency of vibration for a two atom functional group can be calculated approximately by applying Hooke's law for simple harmonic motion. The reader is referred to a book by Harley and Wiberley. (4)

Experimental:

Materials-

The aluminum metaphosphate, aluminum orthophosphate, aluminum dihydrogen phosphate, potassium metaphosphate and sodium tetrametaphosphate samples are products of the Victor Chemical Co. (Chicago, Illinois). The sodium dihydrogen phosphate sample is supplied by J. P. Baker Chemical Co. (New Jersey). The sodium ortho phosphate di ammonium hydrogen phosphate and ammonium dihydrogen phosphate samples are manufactured by Baker and Adamson Chemical Co. (New York, New York). The disodium hydrogen phosphate and sodium pyrophosphate samples are produced by Mallinckrodt Chemical Co. (Philadelphia, Pennsylvania).

The aluminum dihydrogen phosphate is received as a 50% water solution. This solution is evaporated to dryness at 70°C and 110°C. Two water solutions of aluminum dihydrogen phosphate produced by Monsanto Chemical Co. (St. Louis, Missouri) are examined after drying. A technical grade of aluminum orthophosphate manufactured by Baker and Adamson (New York, New York) in 1934 is examined.

The aluminum pyrophosphate is made by reacting sodium pyrophosphate with aluminum chloride as reported by Mellor.(8)

$$3\ Na_4P_2O_7 + 4\ AlCl_3 \longrightarrow Al_4(P_2O_7)_3$$

The alkylation catalyst is prepared as follows: A weight of five hundred grams of 0.125 inch activated alumina pellets (Harshaw Chemical Co. "Purlox") is digested for two hours in a boiling solution of three hundred grams of aluminum nitrate in four hundred grams of water. Distilled water is added as needed to keep the pellets covered with solution. The mixture is allowed to cool overnight, and the supernatant liquid is drawn off through a fine nichrome gauze. A solution, containing 92 g. of di ammonium hydrogen phosphate in four hundred grams of water, is added to the drained pellets, and the mixture is digested for four hours at 50°C. The loose slurry and supernatant liquid are drained as completely as possible through a gauze, and the impregnated pellets dried at 110°C. The impregnated catalyst is activated by heating for eight hours at 600°C. Samples of the aluminum phosphates are activated in the same manner.

Preparation of Infrared Samples:

Several methods for preparing samples are examined. The sedimentation method of Hunt and associates(5) for obtaining samples of very small particles is used in spectrum no. 21, found in the appendix. The particles aggregated on drying and cannot be separated by grinding in a mortar. The advantage of the method is lost. The concentration of the sample in potassium bromide is varied in spectrum no. 7. The .5% sample, one milligram of sample in two hundred milligrams of potassium bromide, gives a good spectrum. Smaller percentages are difficult

to handle and do not increase the resolution of the absorption peaks sufficiently.

The following method for preparing the samples is used in the majority of the spectra:

A weight of one milligram of sample is ground in a mortar with two hundred milligrams of infrared grade potassium bromide. After sifting all of the mixture through a two hundred mesh screen, particle diameter 127u, the mixture is pressed, in an encacuated die, into a self-supporting disk .51-.56 mm thick and 13.03 mm in diameter, under a pressure of 5,000 p. s. i. for four to five minutes.

Spectrometer:

The spectra are all measured with a Perkin-Elmer, Model 21, double beam spectrometer equipped with a sodium chloride prism. The spectrum from two microns to fifteen microns is recorded at a scanning rate of 36.7 seconds per micron. The spectral slit width at 2u is 15.5u and at 15u is 537u. A 200 mg pellet of pure potassium bromide is placed in the reference beam during all runs.

Discussion of Results:

The infrared spectra of several potassium, sodium and ammonium phosphates are examined. The principle absorption bands are listed in Table I. The spectra are very similar to those obtained by Miller and Foil[9] and Corbridge and Lowe.[1] The spectra contain no absorption bands other than water due to the medium in which they were run.

When infrared spectra of compounds containing adsorbed ammonium ions are run in potassium bromide the location of the ammonium ion absorption peak is different than when the same compounds are run as dry powder. In dry powders the absorption peak is at 6.8-6.9u, in potassium bromide the peak is at 7.15-7.25u. The shift occurs because an ion exchange takes place between the sample containing adsorbed ammonium ion and the potassium bromide. The spectrum is recording the energy absorption of ammonium bromide.[3]

Variation in the quality of the spectra of the aluminum phosphates is observed. Aluminum metaphosphate gives the sharpest bands, while the bands of aluminum orthophosphate are broad. The quality of the spectrum varies between samples of the same compound from different companies. This is observed on comparing spectra no. 2 and no. 23 of aluminum orthophosphate and spectra no. 1 and no. 21 of aluminum dihydrogen phosphate. The variations are most likely due to differences in the type

of crystal structure, degree of hydration and method of manufacture.

The infrared spectra of the aluminum phosphates parallel those of the other similar phosphates. Changing the cation causes shifts in the location of the absorption bands of the particular phosphorus ion being studied. The shifts arise from changing the atomic radii, crystal arrangement and type and extent of hydration. The principle absorption bands of the compounds investigated are summarized in Table I and suggested structural formulas for the compounds are given in Table II. the following correlations between molecular structure and absorption wavelength are made with the assistance of papers by Miller and Feil, and Corbridge and Lowe.(1,9)

All the aluminum phosphates being investigated show absorption bands near 3u and 6u. These absorptions are due to water hydration and atmospheric moisture. The stretching of the -O-H bond occurs at 3u and the bending at 6u.

Aluminum orthophosphate shows an absorption at 3.22u which is due to hydrogen bonded water. The absorptions at 8.7-8.8u, 9.1-9.2u, 9.45u and 9.8u are -P-O- vibrations. The shoulder at 8.5 is due to -P-O- bonds with a shorter bond distance. The peak at 12.08 is thought to be due to an -O-P bond under the influence of an attached aluminum atom.

Table I.

Position and Intensities of Infrared Absorption Bands

ABBREVIATIONS:

s - strong	sb - strong and broad
mb - medium and broad	m - medium
wb - weak and broad	w - weak
vsb - very strong and broad	vs - very strong
sh - shoulder	

AMMONIUM di HYDROGEN PHOSPHATE

$NH_4H_2PO_4$

3.05	m
3.4	m
4.05-4.18	w
6.9	m
7.1	m
7.75-7.85	m
7.95	sh
9.0-9.15	mb
9.25-9.35	sh
9.65	w

di AMMONIUM HYDROGEN PHOSPHATE

$(NH_4)_2HPO_4$

3.05	m
3.25	m
3.42	s
3.5	w
4.2	sh
4.5	m
5.15	m
5.83	m
6.0	w
6.6	m
6.85	s
7.12	m
9.25-9.5	sb
9.7-9.85	sh
10.5	m
11.13-11.25	m

POTASSIUM meta PHOSPHATE

KPO_3

2.91	sh
3.0	w
3.1	w
6.25-6.5	sh
7.75	m
7.85	m
8.72	m
9.05-9.3	mb
9.4	sh
9.8	m
9.5	sh
9.6	sh
11.2	wb
12.1-12.4	sh
13.14	m
14.8	s

di SODIUM HYDROGEN PHOSPHATE

$NA_2HPO_4 \cdot 7H_2O$

2.98	m
3.42	s
4.15	m
5.5-5.7	mb
6.0	w
6.85	m
7.36	m
8.65	vs
8.95	m
9.35-9.4	vs
10.5	vs
11.15	vs

Table I. con't.

ABBREVIATIONS:

s - strong
mb - medium and broad
wb - weak and broad
vsb - very strong and broad
sb - strong and broad
m - medium
w - weak
vs - very strong
sh - shoulder

SODIUM ortho PHOSPHATE

$Na_3PO_4 \cdot 12H_2O$

2.98	m
3.42	w
6.85	w
9.5-9.8	sb
9.1-9.25	sh
11.4	w

SODIUM tetra meta PHOSPHATE

$(NaPO_3)_4 \cdot 4H_2O$

2.91 2.98	m
6.05	m
7.8	s
7.95	sh
9.05	s
9.8-10.1	sb
13.2-13.5	mb
14.38	wb

SODIUM di HYDROGEN PHOSPHATE

$NaH_2PO_4 \cdot H_2O$

2.98	mb
3.42	s
4.1-4.2	w
6.0	mb
6.85	m
7.3	w
8.65	m
9.10-9.75	sb
10-10.4	sh
10.8-11.15	sh

SODIUM pyro PHOSPHATE

$Na_4(P_2O_7) \cdot 10H_2O$

2.92	sb
3.0	sh
3.3	w
3.42	w
4.4	wb
5.75	w
6.02	m
6.5	w
6.87	w
7.3	w
8.98-9.05	sb
9.8	m
10.05	w
10.9	mb

ABBREVIATIONS:

s - strong	sb - strong and broad
mb - medium and broad	m - medium
wb - weak and broad	w - weak
vsb - very strong and broad	vs - very strong
sh - shoulder	

ALUMINUM PYRO PHOSPHATE

$AlPO_4 \cdot X\ H_2O$

2.95	s
3.22	s
6.05	s
8.5	sh
8.7-8.8	sh
9.1-9.2	sh
9.45	vs
9.8	s
12.08	sb
13.6-13.9	sh
14.3-14.7	mb

ALUMINUM di HYDROGEN PHOSPHATE

$Al(H_2PO_4)_3$

2.75	m
3.5	mb
4.2-4.35	mb
5.9	mb
6.0-6.05	sh
7.6	sh
8.08	vs
8.3	vs
8.6	vs
8.9	vs
9.55; 9.68	vs
10.14-10.25	vsb
12.9	m

ALUMINUM meta PHOSPHATE

$Al(PO_3)_3$

3.0	mb
3.4-3.5	m
6.1-6.3	mb
6.35	sh
6.55	sh
7.68	vs
7.82	vs
8.48	s
8.78	vs
9.25	sh
9.45	vs
9.78	vsb
12.38	m
13.6	vs
13.9	s

ALUMINUM pyro PHOSPHATE

$Al_4(P_2O_7)_3$

2.92	s
3.0	sh
8.55-8.75	vsb
8.9	sh
9.3	sh
10.5	mb
12.1	w
13.8-13.5	wb

Aluminum metaphosphate shows an absorption at 3.4-3.5u which is due to _O_H stretching of water molecules hydrogen bonded to the compound. The strong peaks at 7.68u and 7.82u are caused by _P=O vibrations, in a tri or tetra cyclic polymer. The peak at 8.48 is due to the stretching of a shortened _P_O bond in a linear polymer. The bands at 8.78u, 9.45u, and 9.78u are due to _P_O stretching. The absorption at 12.38 is thought to be due to an P_O_ bond under the influence of an attached aluminum atom. The bands at 13.6u and 13.9u are due to the cyclic _P_O_P_ bond vibrations. The spectrum agrees very well with the aluminum tetrametaphosphate of Corbridge and Lowe.(1)

The sharp absorption peak of aluminum dihydrogen phosphate at 2.75u is due to _O_H stretching free from the affects of hydrogen bonding. The absorptions at 3.5u, 7.6u, 4.1-412u, 8.08u are due to _P_OH stretching vibrations. The band at 8.3u is due to a _P=O vibrations. Various _P_O_ vibrations give rise to absorptions at 8.6u, 8.9u and 9.48-9.7u. The peak at 10.04-10.35u is due to _P_OH bending. The band at 12.9u is thought to be an P_O_ under the influence of an aluminum atom.

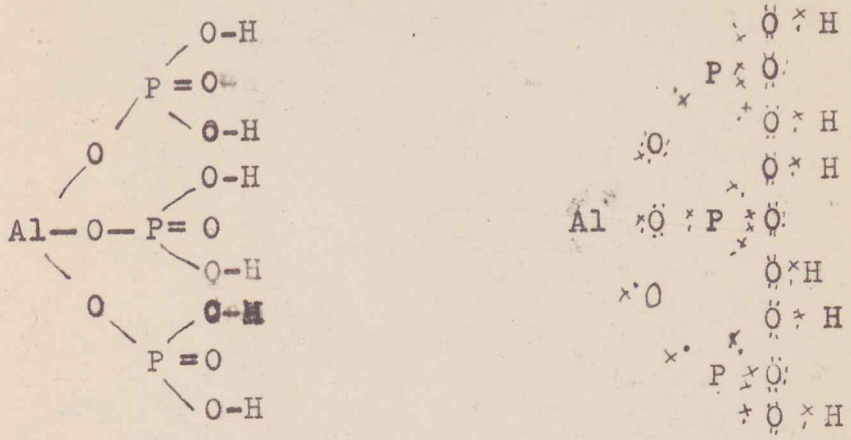
Aluminum pyrophosphate spectrum shows absorptions at 8.55-8.75u, 8.9u and 9.37 due to _P_O_ vibrations. The absorptions at 10.5u and 12.8-13.5u are caused by _P_O_P_ stretching. The weak peak at 12.3u is thought

Table II

Kekulé and Electronic Formulas of Aluminum Phosphate Compounds

Aluminum ortho Phosphate

Aluminum di Hydrogen Phosphate



cyclic Aluminum meta Phosphate

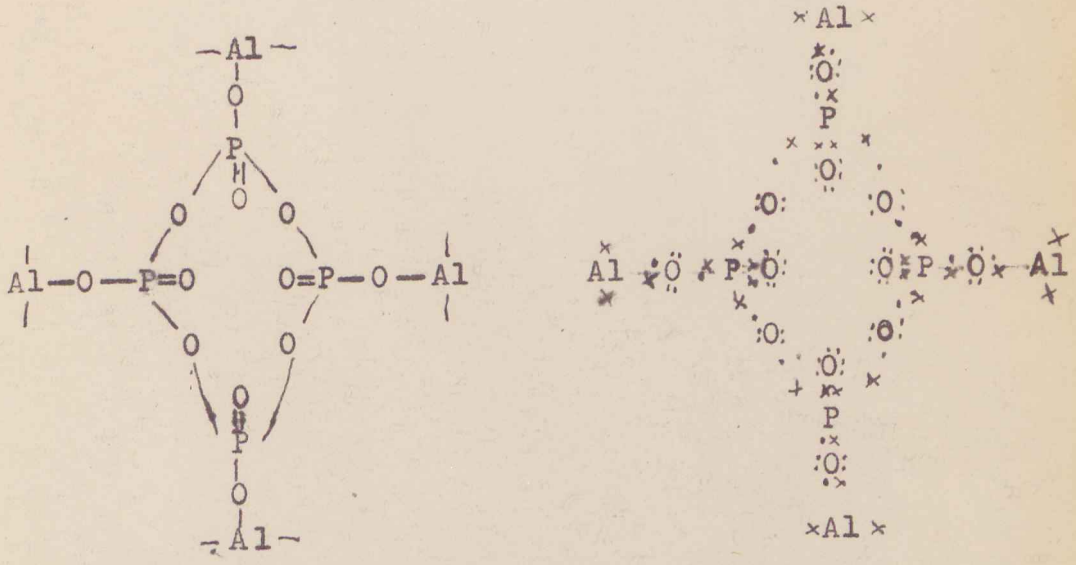
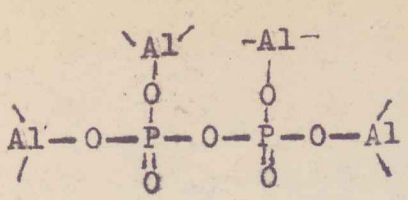
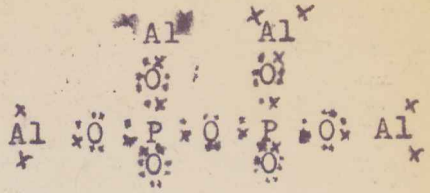


Table II (cont.)

Aluminum pyro Phosphate





to be the -P-O- bond under the influence of an aluminum atom.

The spectra of the aluminum oxide support and the alumina-aluminum phosphate catalyst do not contain well defined absorption bands in the unactivated or activated state. The powder which falls off the activated or unactivated catalyst on sifting contains only a small percentage of catalyst support and give a fair spectrum.

The catalyst support has absorption peaks at 2.9u, 3.5u and 6.15u corresponding to the various absorptions of adsorbed water. There are general areas of absorption at 9.4-10.1u and 12.2-15u. These areas may be caused by the vibrations of the covelant aluminum oxygen bonds.

The spectra of the catalyst and catalyst siftings seems to indicate that the phosphate part of the catalyst, before activation, is mostly aluminum orthophosphate. The strongest absorption peak for the catalyst is at 8.7-9.3u, which corresponds to the strongest peak for aluminum orthophosphate.

Support for the theory that aluminum orthophosphate is formed when the catalyst is produced can be gained from the reaction equations and the relative solubility of the various aluminum phosphate salts.

(1) $(NH_4)_2HPO_4 + Al_2(NO_3)_3 \xrightarrow{Al_2O_3}$

$$2\ NH_4^+ + HPO_4^{-2} + Al^{+3} + 3\ NO_3^-$$

(2) $H^+ + HPO_4^{-2} \xrightarrow{HOH} H_2PO_4^-$

(3) $H_2PO_4^- \longrightarrow H^+ + HPO_4^{-2}$ $\quad K_1 = 6.2 \times 10^{-8}$

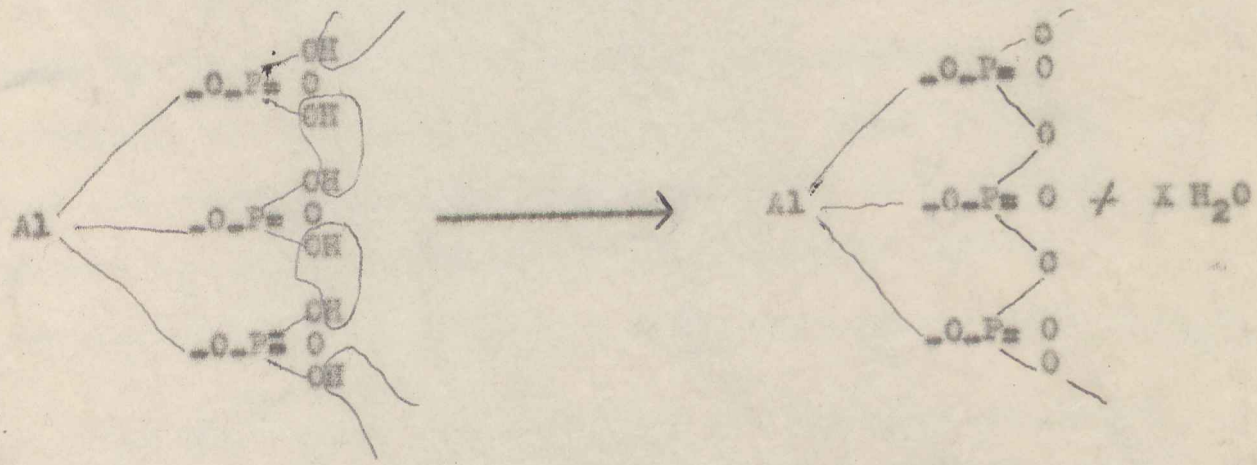
(4) $HPO_4^{-2} \longrightarrow H^+ + PO_4^{-3}$ $\quad K_1 = 1 \times 10^{-12}$

Due to the ionization constants of equations (3) and (4) a small amount of phosphate ion should be formed. There is a large excess of aluminum ions and the alumina pellets can act as "seeds" for precipitation. Aluminum orthophosphate is very insoluble. Aluminum dihydrogen phosphate is fairly soluble and aluminum hydrogen phosphate is probably very soluble because it is not reported in the literature as a pure compound. The reaction solution is found to be very acid. The excess aluminum ions precipitate the phosphate ions as soon as they are formed. This forces equation$_{(4)}$ to the right which brings equation$_{(3)}$ to the right. A large excess of hydrogen ion is therefore generated.

Aluminum dihydrogen phosphate undergoes a radical change when activated. The intensity of the whole spectrum decreases; all the absorption bands before 7u become unintelligible. A new absorption peak appears at 7.82u, due to strong -P=O vibrations. A -P-O-P- vibration gives

rise to a new peak at 10.4u. An intensification of a band at 9.1u occurs due to an increase in a type of -P-O- bond vibration. The bands at 8.3u, 8.6u and 8.9u are reduced. The bands due to -P-OH bond vibrations at 7.6u and 8.08u become unintelligible. The following shifts in absorption peaks occur: 7.1u to 7.04u, 10.14-10.25 to 9.9-10.05, and 12.9u to 12.4u. The over all spectrum resembles that of a mixture of linear and cyclic metaphosphates.

The coversion of dihydrogen phosphates to metaphosphates is reported by Latimer and Hildebrand.(5)


Al
OH
O
O
O

due to meta type -P=O vibrations. A very strong and broad band appears at 13.7u and 14.05u due to formation of cyclic P-O-P bonds. The linear -P-O-P- bond absorption band at 10.5u is greatly reduced and blocked by the extra broad band centered at 8.9u. The very strong peak at 8.55-8.75u is intensified and slightly shifted to 8.6-9.1u. A weak peak appears at 12.35u. When the aluminum pyrophosphate is activated, the absorption peak at 3.5u is greatly intensified indicating an increase in the hydrogen bonding of the adsorbed water, $Al_4(P_2O_7)_3 \longrightarrow 2\ Al(PO_3)_3 + Al_2O_3$

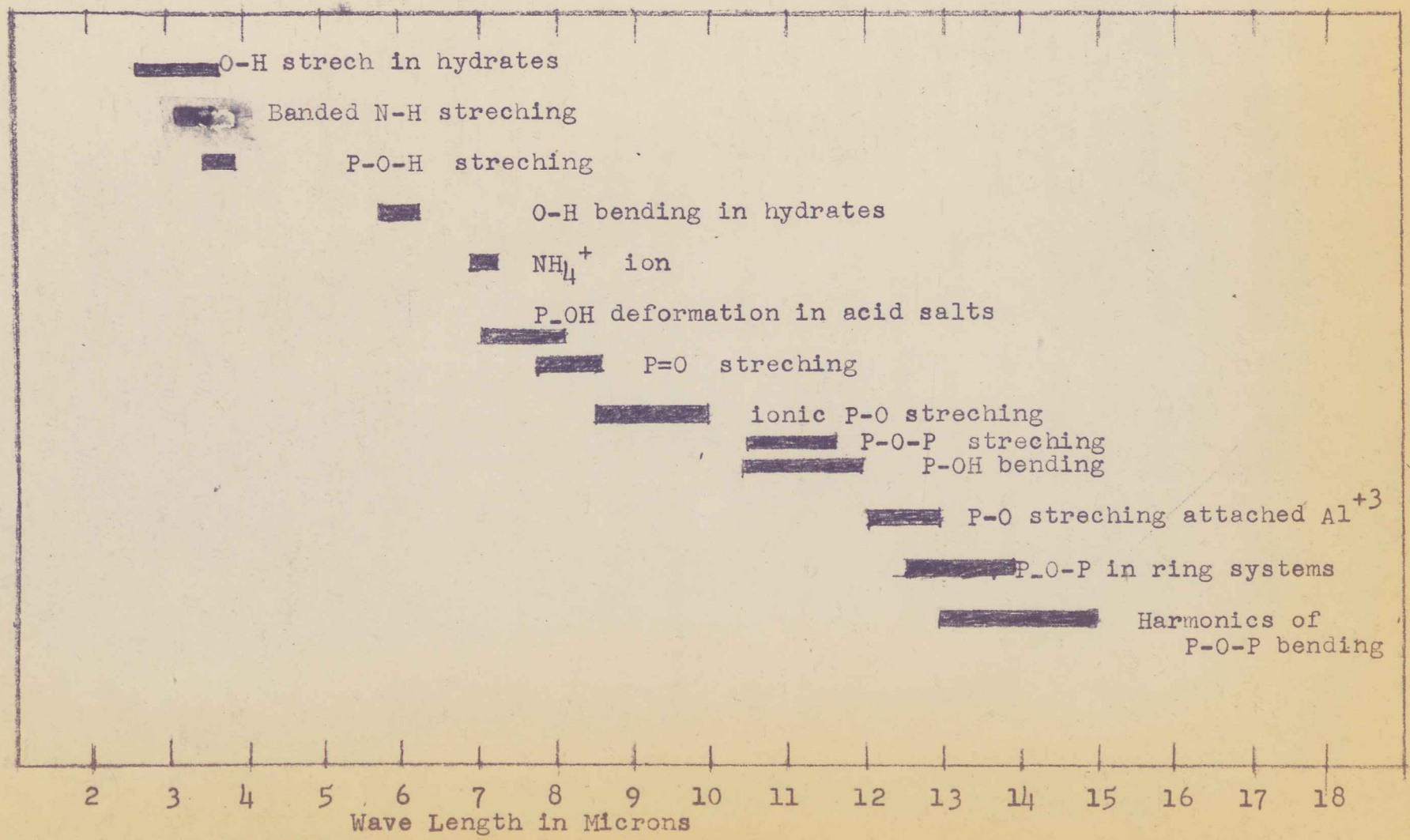
When aluminum orthophosphate is activated all peaks below 7u are reduced and very strong bands appear at 8.55-8.7u, 8.8-8.9u and 13.9-14.1u. These peaks indicate that the orthophosphate is probably converted to a mixture containing mostly pyrophosphate and some metaphosphate.

$$6\ AlPO_4 \longrightarrow Al_4(P_2O_7)_3 + Al_2O_3 \longrightarrow 2\ Al(PO_3)_3 + Al_2O_3$$

Upon activation of the catalyst and the catalyst siftings a conversion similar to that of aluminum orthophosphate is believed to take place. The absorption bands at 2.9u, 3.5u and 6.15u are slightly decreased. The absorption band at 8.7-8.9u is increased at 8.85u and decreased from 8.95-9.3u. The activated siftings indicate some absorption at 13.7-14.4u due to the formation of some cyclic -P-O-P- bonds. The strong peaks at 7.25u and 3.2u disappear when the catalyst is activated. These peaks are caused by ammonium ions adsorbed on the surface of the catalyst durings its preparation.

Spectrum number 22 is a mixture of aluminum orthophosphate and aluminum metaphosphate. This spectrum indicates that mixtures of phosphates can be qualitatively identified.

Table III Suggested Characteristic Absorption Bands *



* Tables compiled from papers by Corbride and Lowe and Miller and Foil; (1,2), (9)

Summary:

The different aluminum phosphates give characteristic absorption bands which can be used to identify the pure compounds. It is believed that identification of the components of a mixture of aluminum phosphates is qualitatively possible. Aluminum metaphosphate and aluminum dihydrogen phosphate are the easiest to identify because of their distinct bands. Infrared can be useful tool in the qualitative analysis of unknowns that containing phosphates and other polyatomic ions. Miller and Wilkins find the combination of infrared, emission, and Xray spectroscopy a useful analytical method for inorganic unknowns.(2)

The conversion of aluminum dihydrogen phosphate to a mixture of linear and cyclic metaphosphates is observed. The aluminum orthophosphate is thought to be converted to a mixture of aluminum pyrophosphate and cyclic aluminum metaphosphate.

The alumina-aluminum phosphate catalyst before activation is considered to be mostly aluminum ortophosphate on alumina. After activation the aluminum orthophosphate is probably converted to a mixture of aluminum pyrophosphate, and aluminum metaphosphate.

A great deal of work needs to be done on the technique of using infrared spectroscopy to study the actual alkylation reaction on the surface of the catalyst at high temperatures also the use of self-supporting sample pellets

should be examined.

Bibliography

(1) Corbridge, D. E. C. & Lowe, E. J. "Infrared Spectra of Some Inorganic Phosphorus Compounds", Part I Journal of the Chemical Society, England, pp 493-502, February 1954

(2) Corbridge, D. E. C. & Lowe, E. J. "Infrared Spectra of Some Inorganic Phosphorus Compounds", Part II Journal of the Chemical Society, England, pp 4555-64, December 1954

(3) Kiselena, R. P. and Pliskin, W. A. "The Infrared Spectra of Adsorbed Molecules", Advances in Catalysis and Related Subjects, (Adademic Press, Inc., N. Y. 1958) Vol. X pp. 45

(4) Harley, J. H. and Wiberly, S. E. Instrumental Analysis, (John Wiley and Sons, Inc., N. Y. 1954) pp. 65

(5) Hunt, J. & Wisherd & Bonham "Infrared Absorption of Minerals and Inorganic Compound", Journal of Analytical Chemistry Vol. 22 pp. 1478 December 1950

(6) Lattimer, W. M. and Hildebrand, J. H. Reference Book of Inorganic Chemistry, (Macmillan Co., N. Y. 3rd ed 1951) pp. 232

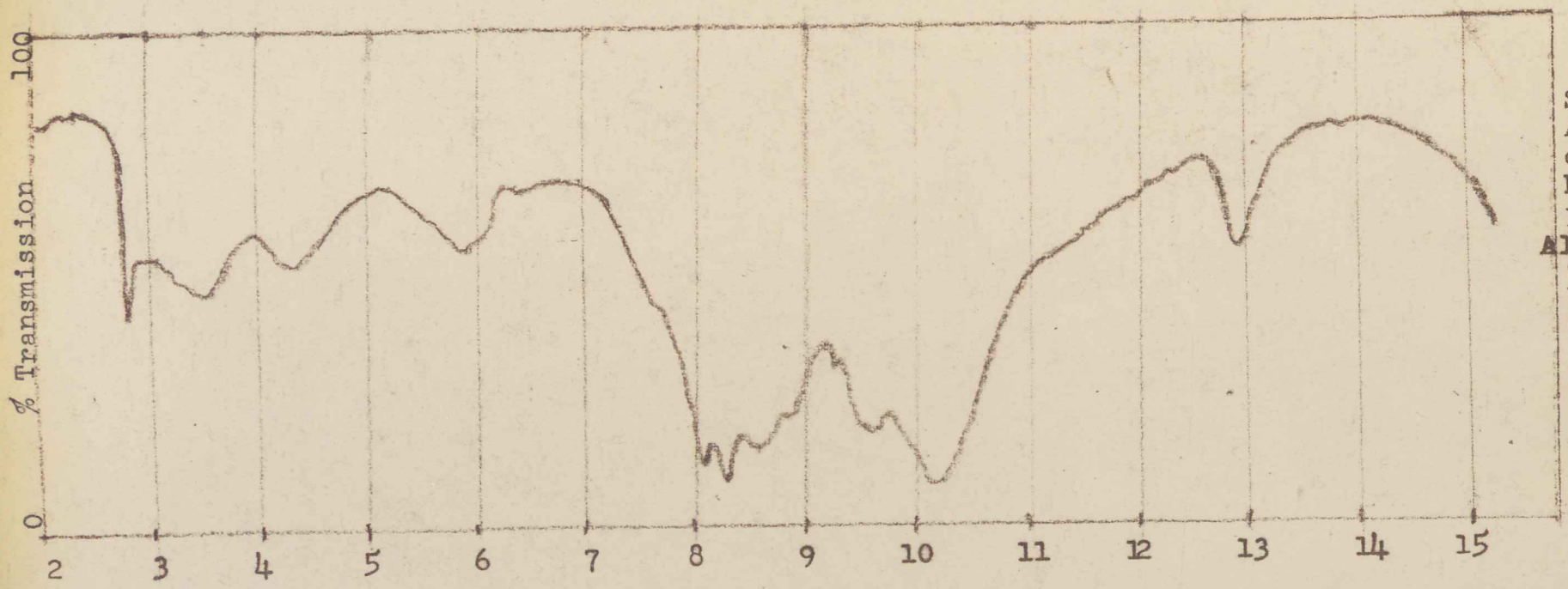
(7) McDonald, R. S. "Surface Fuctionality of Amorphous Silica" 32nd National Colloid Symposium, Preprints of Papers, Journal of Physical Chemistry, June 1921, 1958 pp. 16-26

(8) Mellor, J. W. A Comprehensive Treatise on Inorganic Chemistry, (Longmans & Green Co., N. Y. 1924) Vol. 5 pp. 365

(9) Miller, Foil, A., Wilkins, C. H. "Infrared Spectra and Some Characteristic Frequencies of Inorganic Compounds" Journal of Analytical Chemistry, August 1952 pp. 1253-1293

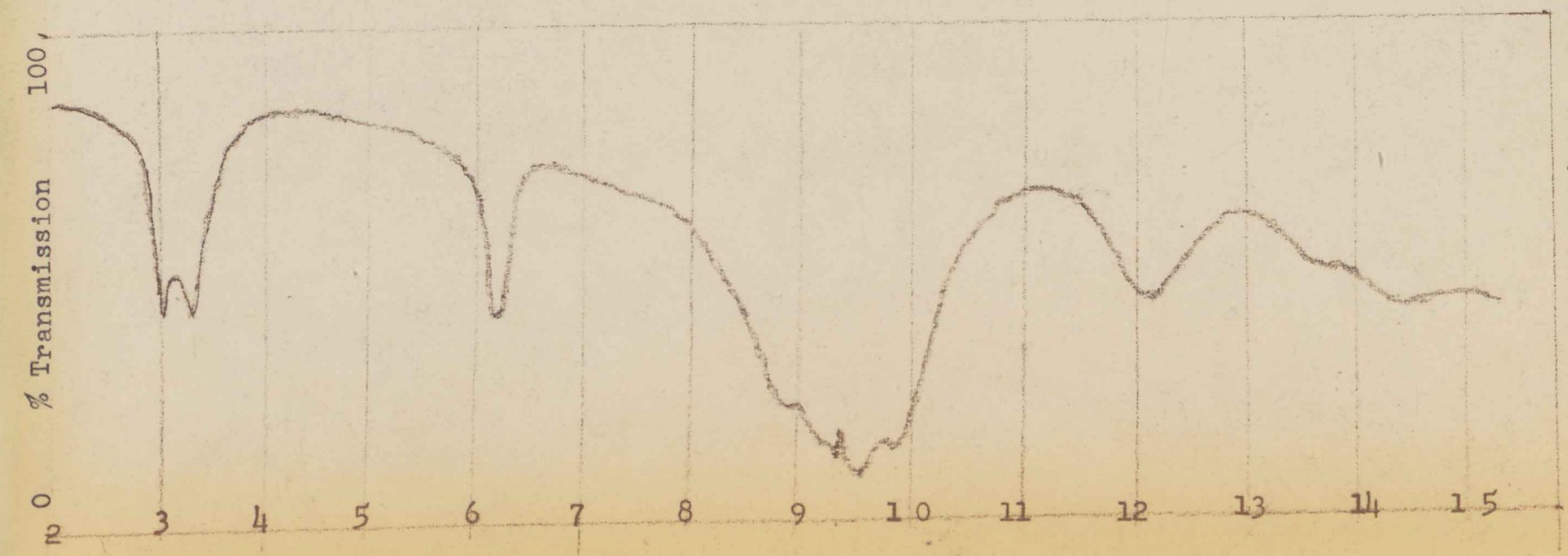
(10) Paskovich, D. "Alkyation of Phenol" Thesis Presented at Union College, Schenectady, N. Y.

APPENDIX



Spectrum no. 1
Sample:
Aliminum di-hydrogen phosphate
$Al(H_2PO_4)_3$
Origin:
Victor Chem. Co.

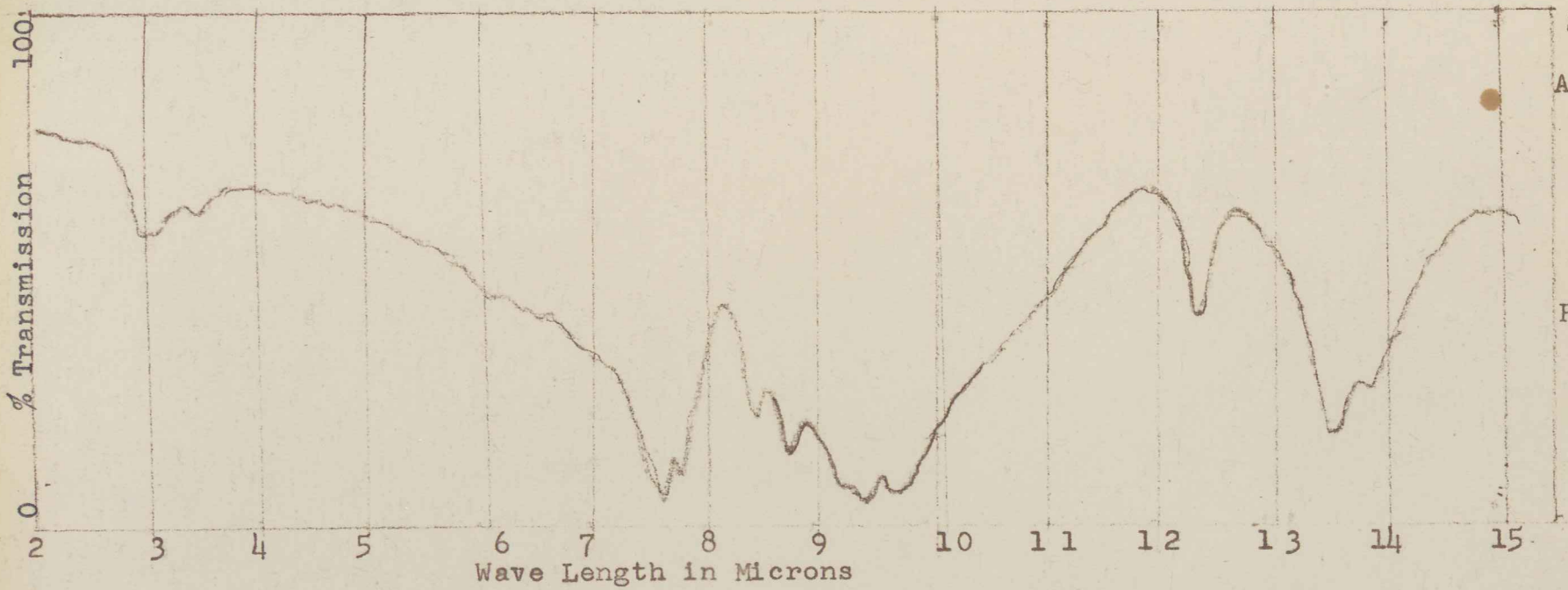
Phase:
in KBr



Spectrum no. 2

Sample:
Aluminum ortho-phosphate
$AlPO_4$
Origin:
Victor Chem. Co.

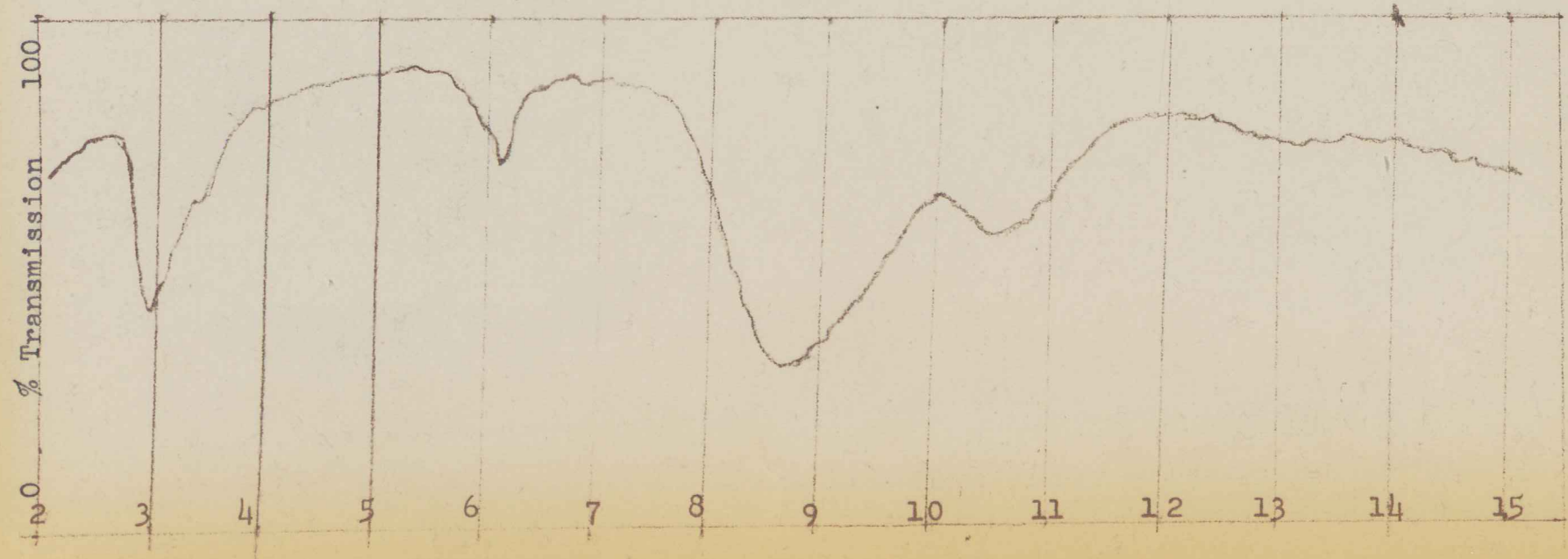
Phase:
in KBr



Spectrum no. 3
Sample:
Aluminum meta phosphate
$Al(PO_3)_3$

Origin:
Victor Chem. Co.

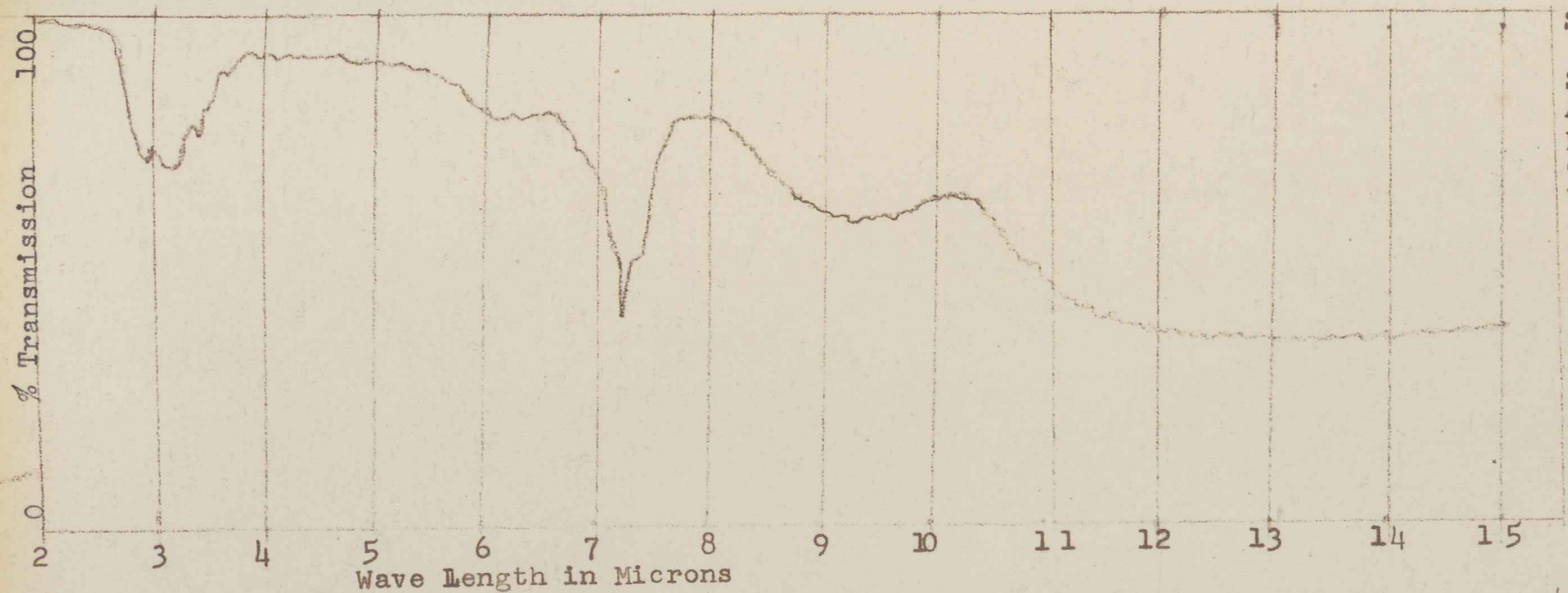
Phase:
in KBr



Spectrum no. 4
Sample:
Aluminum pyro phosphate
$(Al_4(P_2O_7)_3$

Origin:
Mallinckrodt Chem. Co.

Phase:
in KBr.

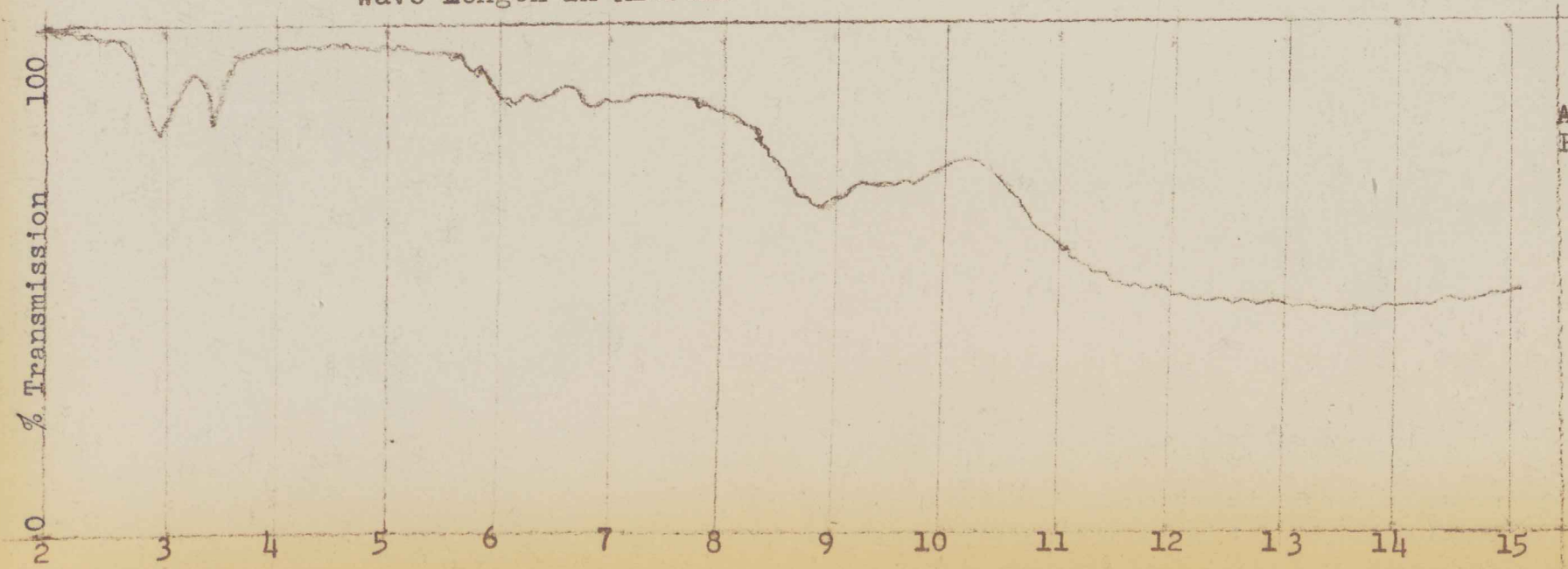


Spectrum no. 5

Sample:
Alumina-Aluminum
phosphate
catalyst
unactivated

Origin:
Lab. Prep.

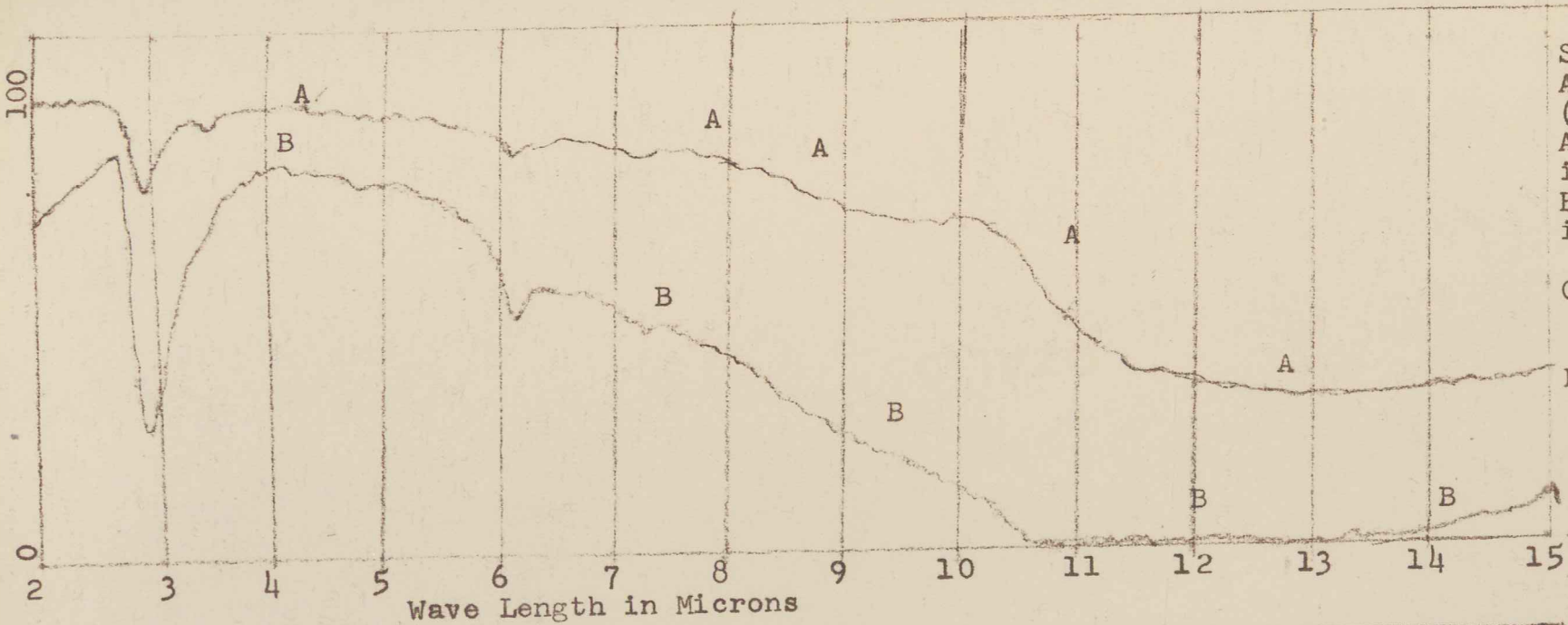
Phase: in
KBr



Spectrum no. 6

Sample:
Alumina-Aluminum
Phosphate
catalyst
activated

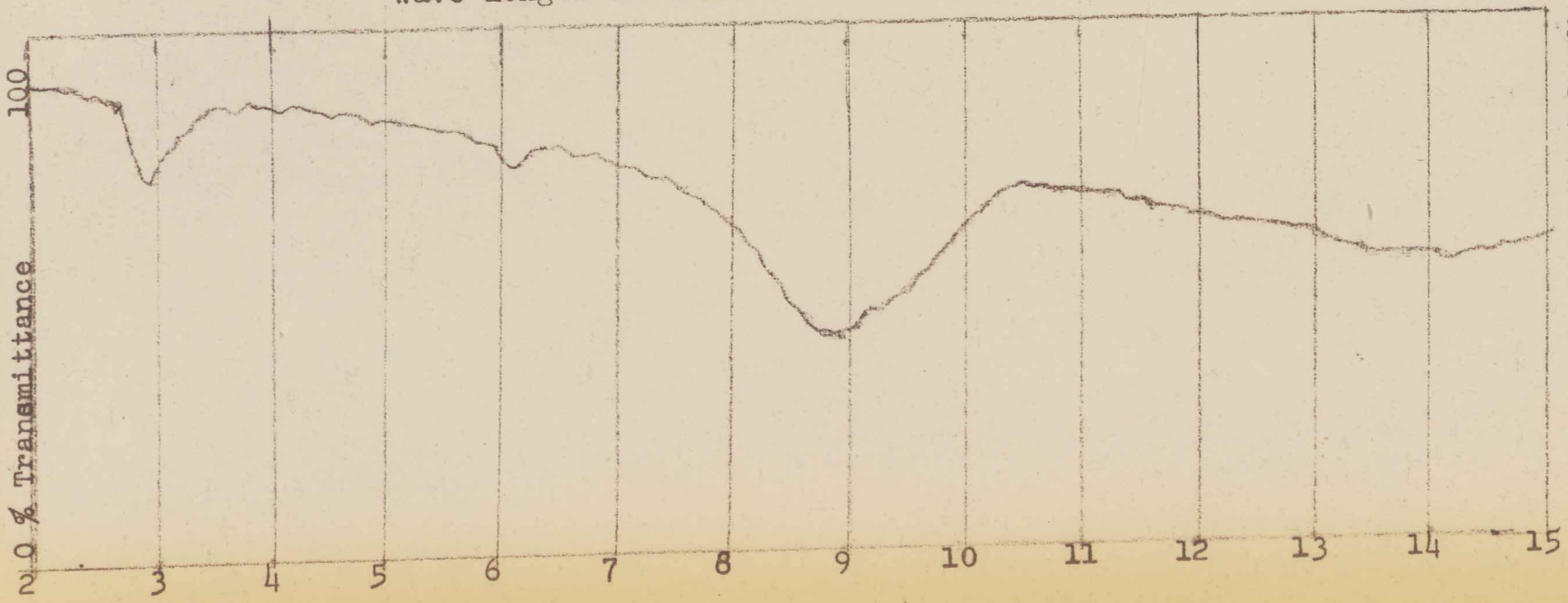
Origin:
Lab. Prep.



Spectrum no. 7
Sample:
Alumina pellets
(purlox)
A. 1mg. sample
in 200mg. KBr
B. 2mg. sample
in 200mg KBr

Origin:
Harshaw Chem.

Phase: in KBr



Spectrum no. 8

Sample:
Activated
residue from
Alumina-
Aluminum
Phosphate
Catalyst

Origin: Lab

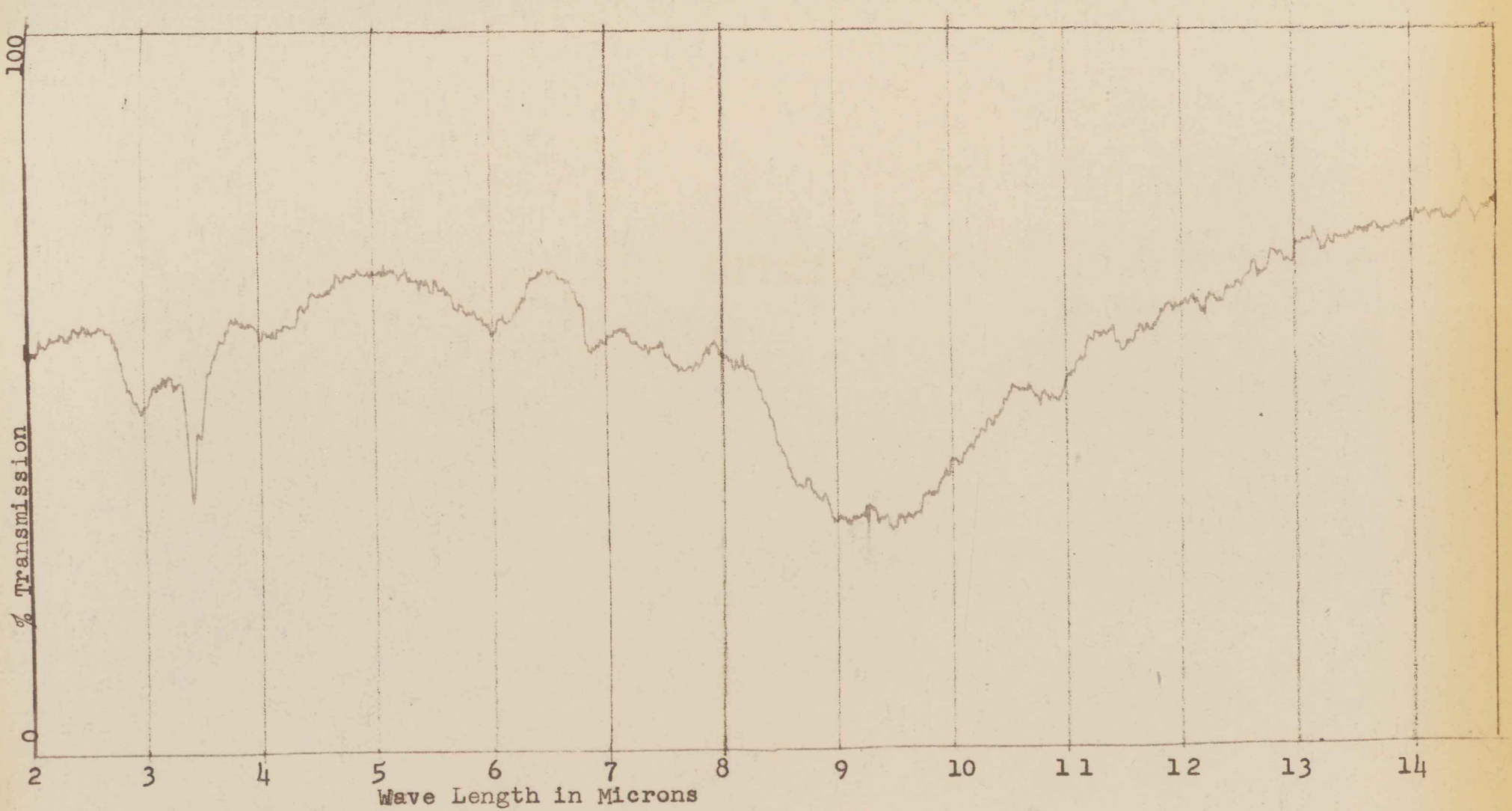
Phase: in KBr

Spectrum no. 9

Sample: di Ammomium Hydrogen Phosphate
$(NH_4)_2HPO_4$

Origin: Baker and Adams Chem. Co.

Phase: in KBr

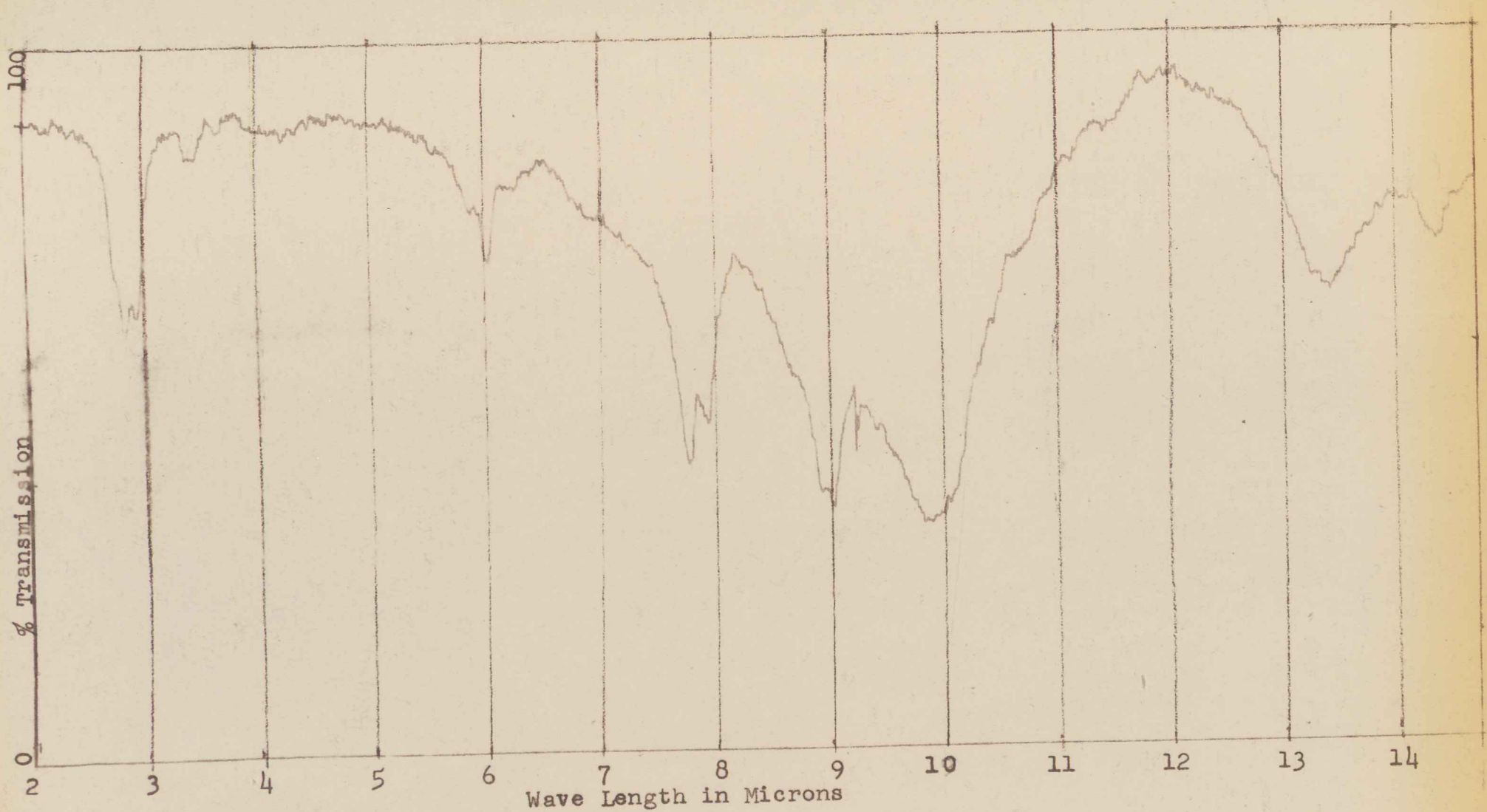


Spectrum no. 10

Origin: Baker Chem. Co.

Sample: Sodium di Hydrogen Phosphate
NaH_2PO_4

Phase: in KBr.



Spectrum no. 11

Sample: Sodium tetra meta Phosphate
$(NaPO_3)_4 \cdot 4H_2O$

Origin: Victor Chemical Co.

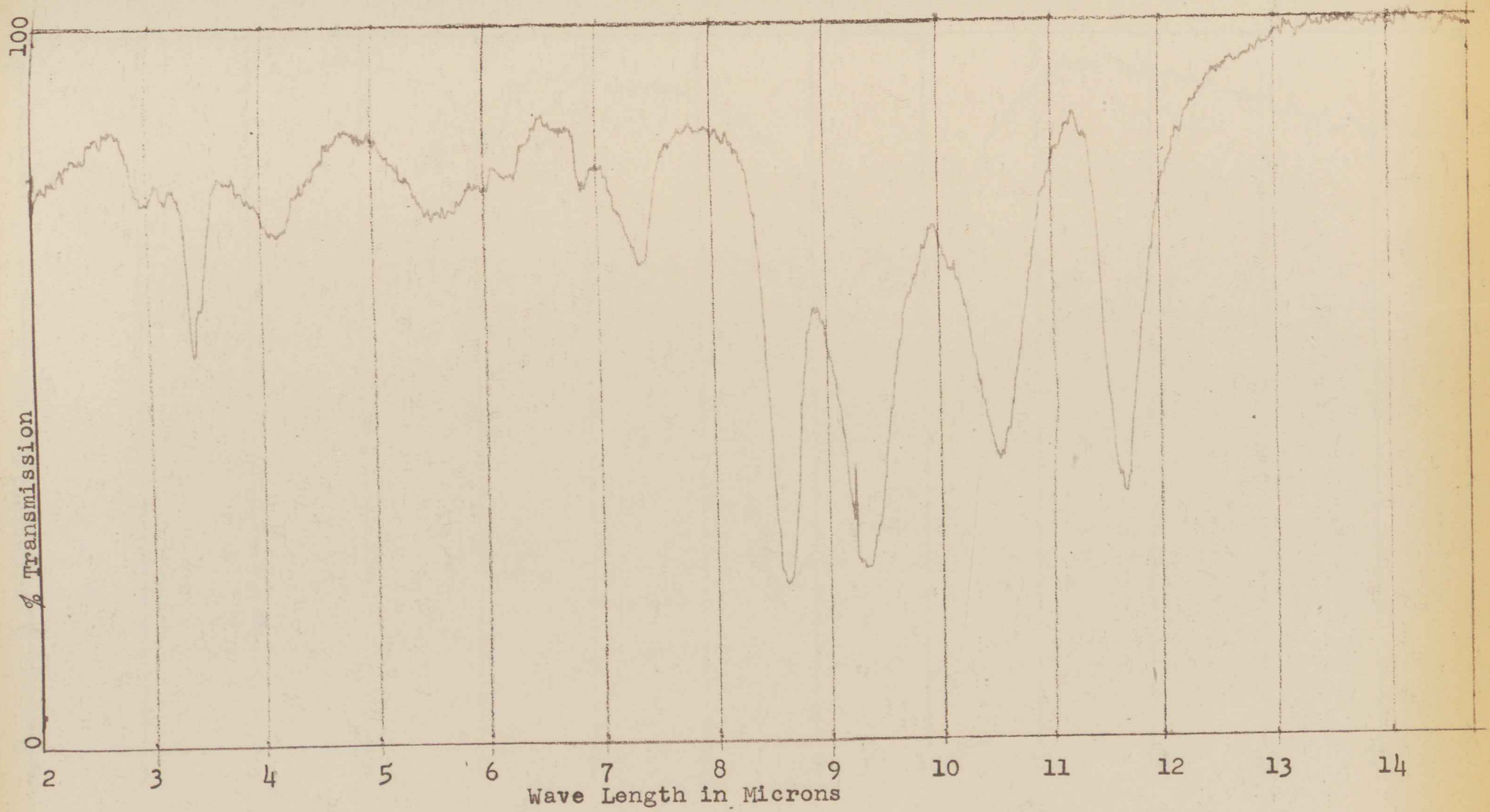
Phase: in KBr

Spectrum no. 12

Sample: Potassium meta Phosphate
KPO_3

Origin: Victor Chemical Co.

Phase: in KBr

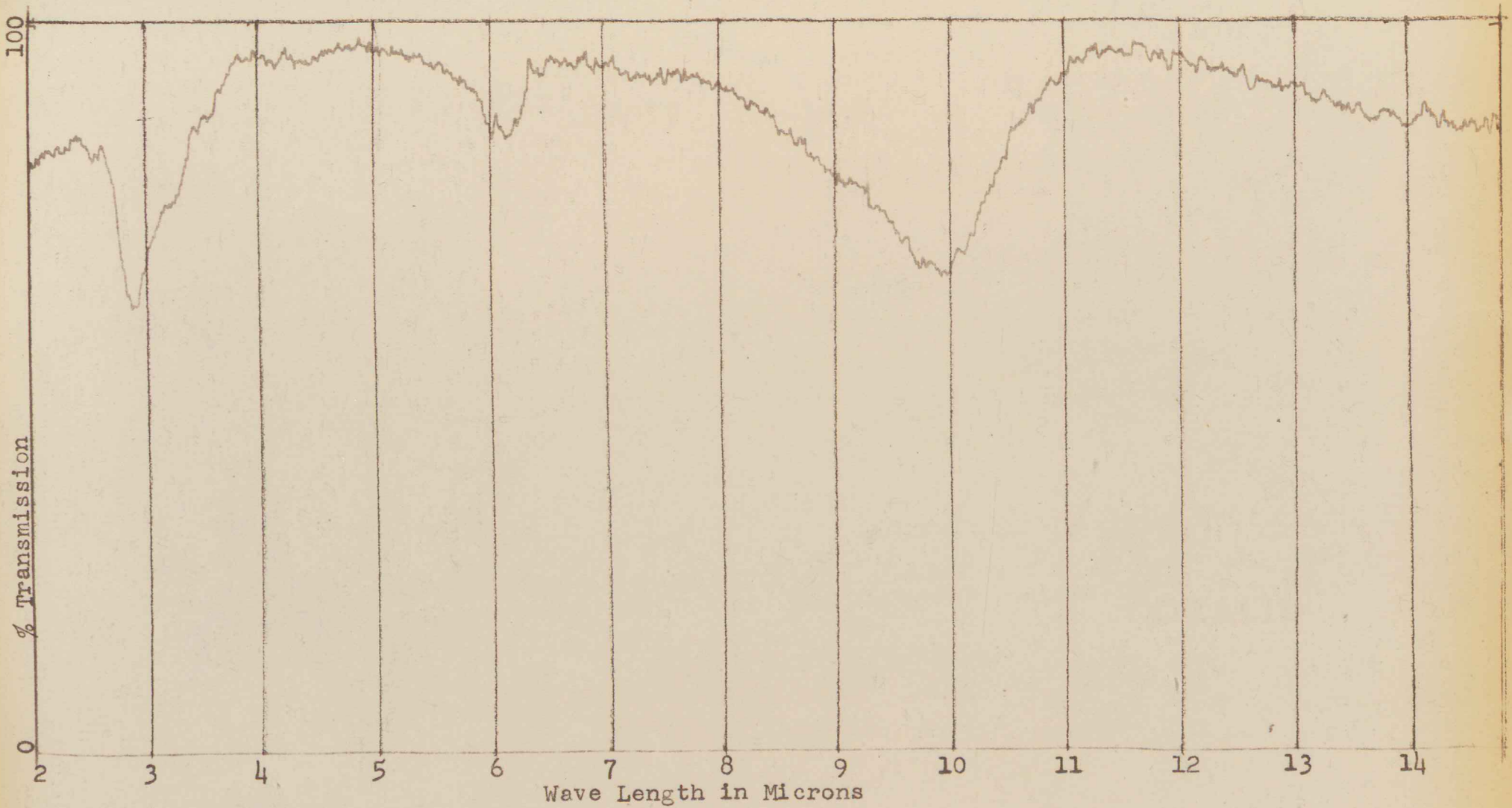


Spectrum no. 13

Sample: di Sodium Hydrogen Phosphate
Na_2HPO_4

Origin: Mallinckrodt Chem. Co.

Phase: in KBr



Spectrum no. 14

Sample: $Na_3PO_4 \cdot 12\ H_2O$

Sodium ortho Phosphate

Origin: Baker and Adamson Chem. Co.

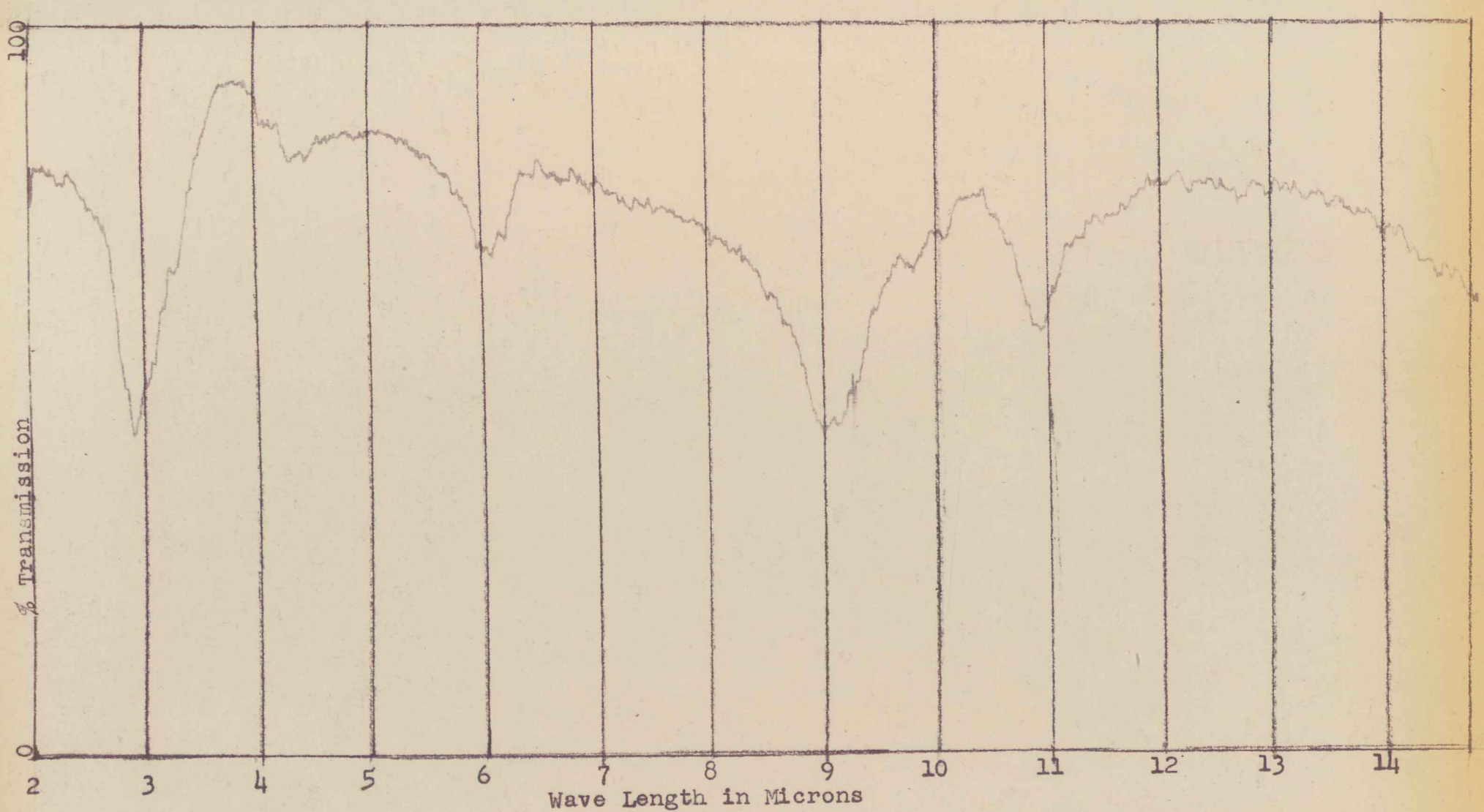
Phase: in KBr

Spectrum no. 15

Sample: Ammonium di Hydrogen Phosphate
$NH_4\ H_2PO_4$

Origin: Baker and Adams Chem. Co.

Phase: in KBr

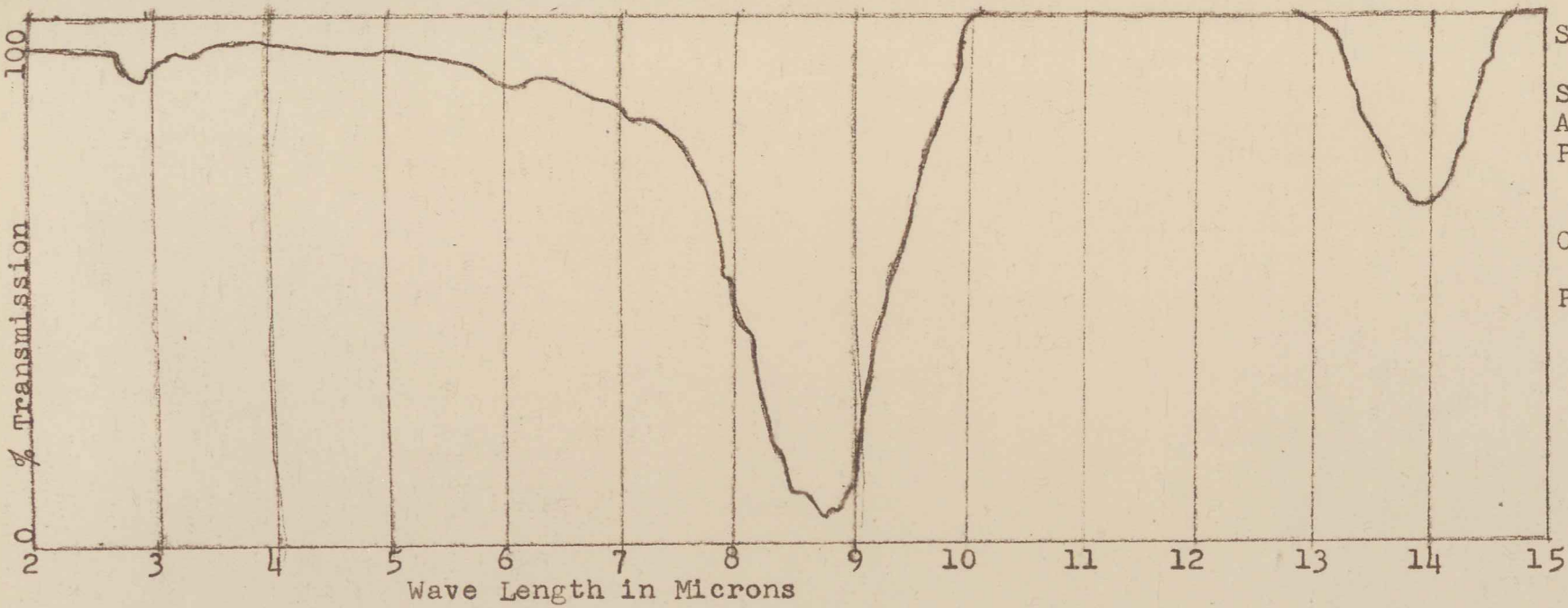


Spectrum no. 16

Sample: Sodium pyro Phosphate
$Na_4P_2O_7$

Origin: Mallenckrodt Chem. Co.

Phase: in KBr

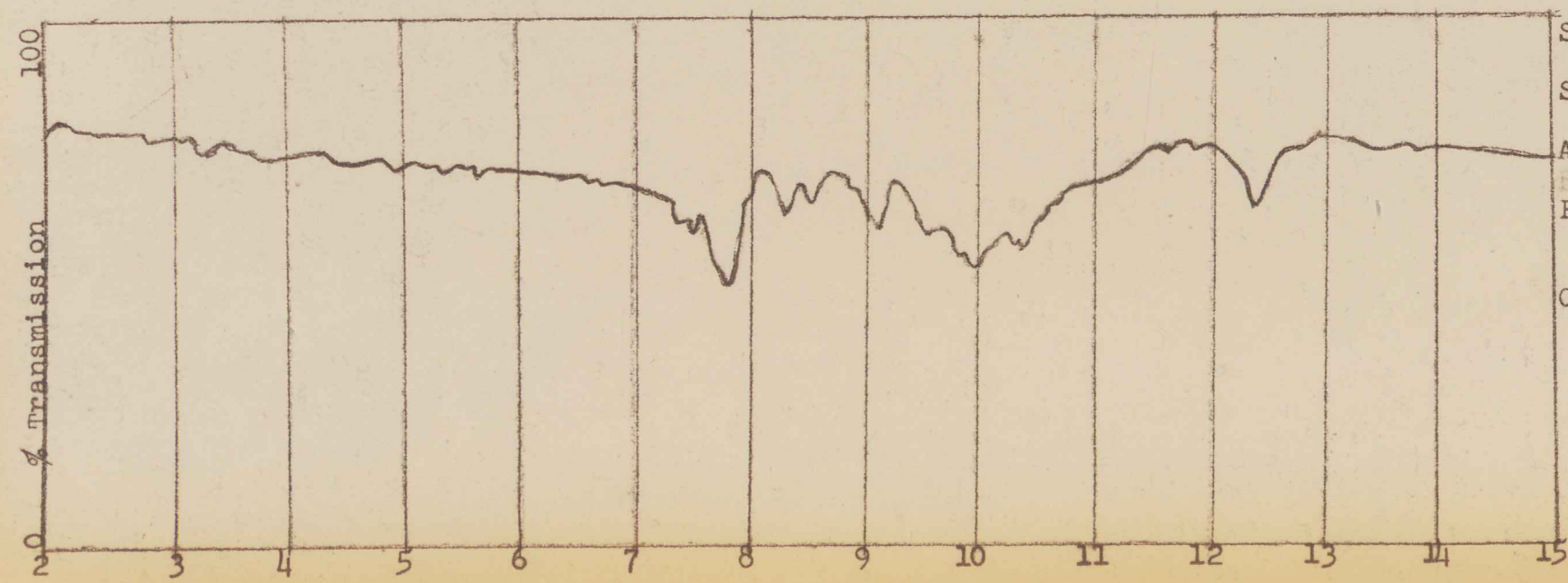


Spectrum no. 17

Sample: $AlPO_4$
Aluminum otho
Phosphate
activated

Origin: Lab.

Phase: in KBr



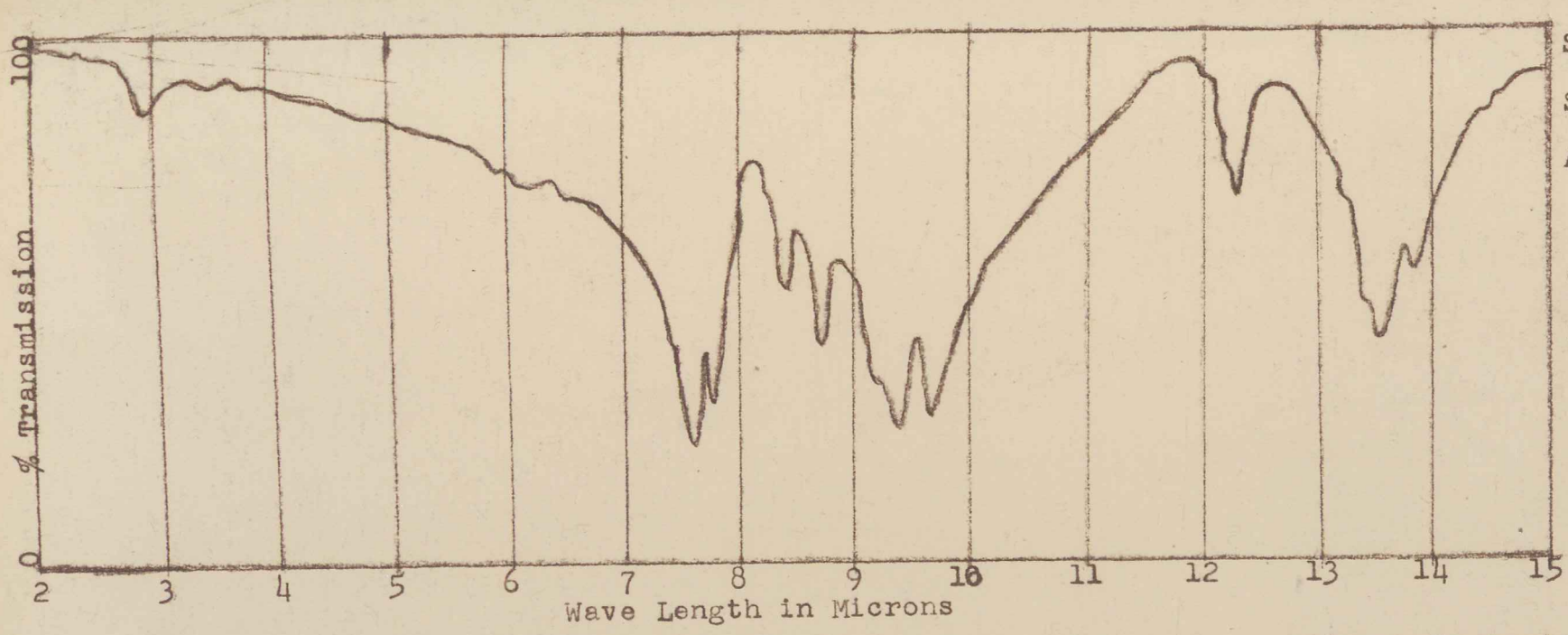
Spectrum no. 18

Sample: AlH_2PO_4

Aluminum di
Hydrogen
Phosphate
activated

Origin: Lab.

Phase: in KBr



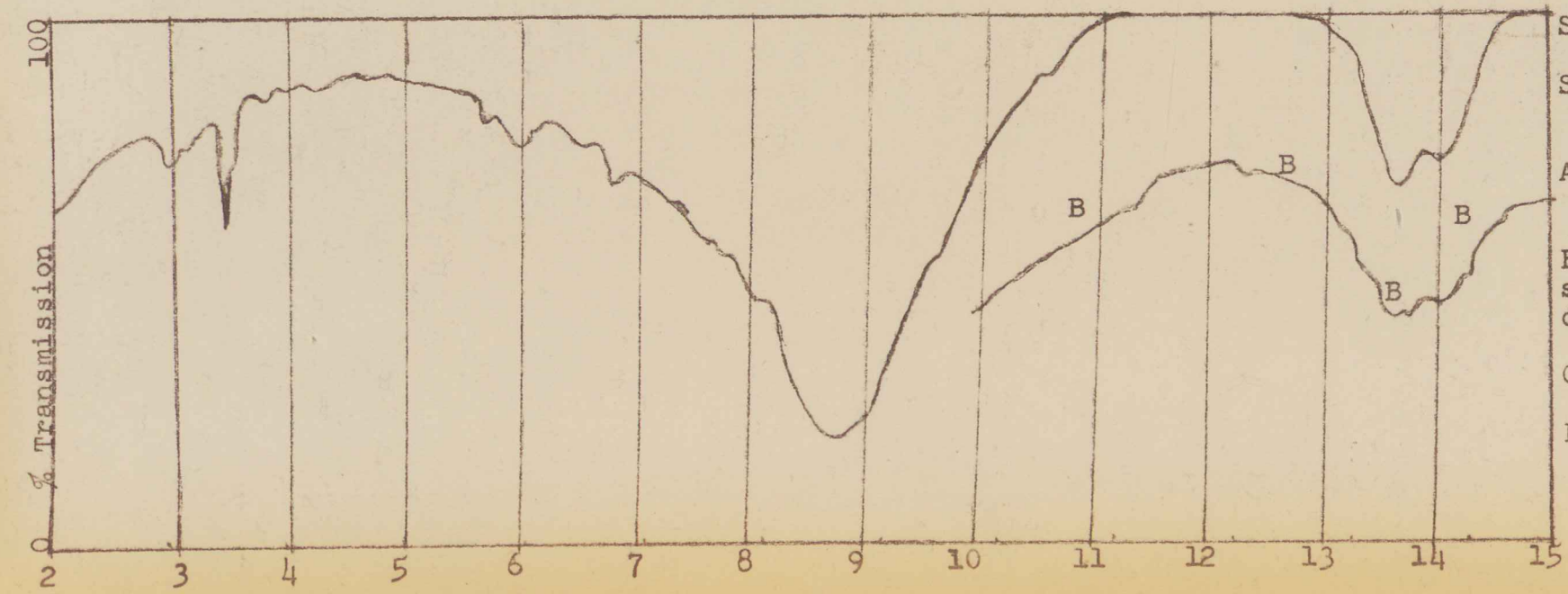
Spectrum no. 19

Sample: $Al(PO_3)_3$

Aluminum meta Phosphate activated

Origin: Lab

Phase: in KBr



Spectrum no. 20

Sample: $Al_4(P_2O_3)_3$

Aluminum pyro Phosphate activated

B intensity of sample beam decreased

Origin: Lab.

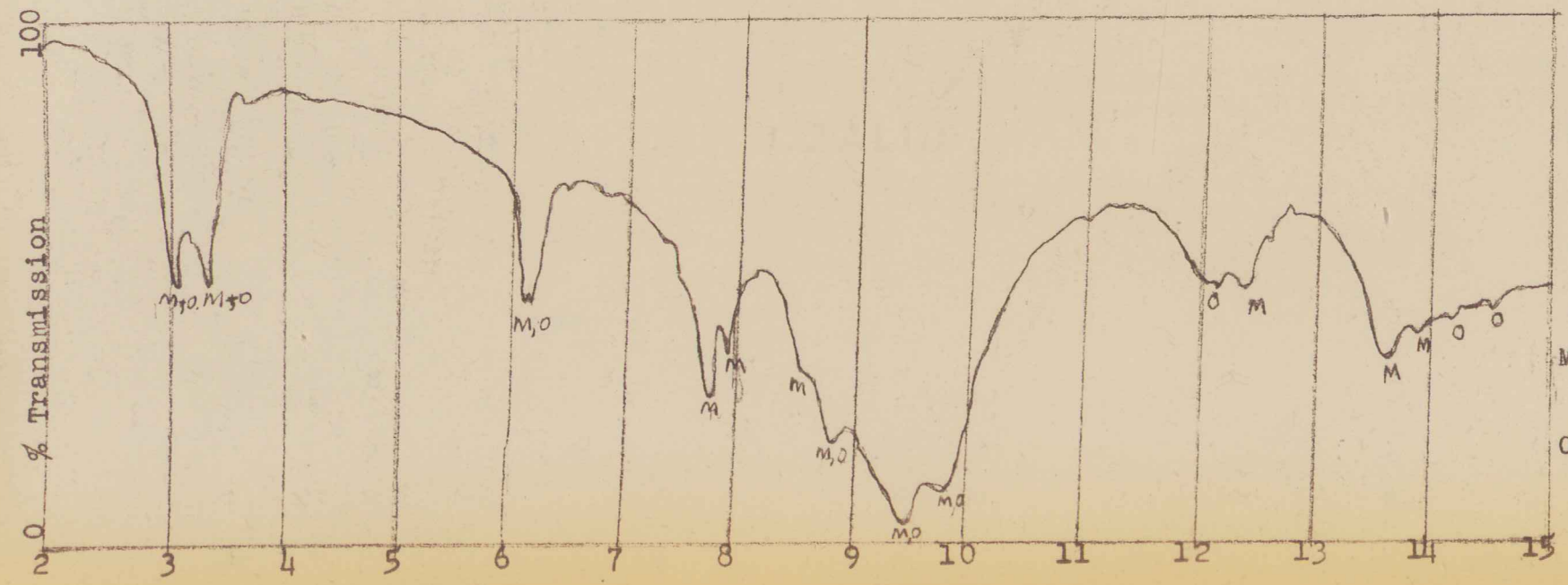
Phase: in KBr

Spectrum no. 21

Sample:
Aluminum di Hydrogen Phosphate
$Al(H_2PO_4)_y$

Origin:
Monsanto Chem. Co. (St. Louis Mo.)

Phase: in KBr



Spectrum no. 22

Sample:
¼ %$AlPO_4$ +
¼% $Al(PO_3)_3$
in 200 mg KBr

Origin: Lab

M meta phosphate

O ortho phosphate

Spectrum no. 23

Sample: Al PO_4

Aluminum orto Phosphate Tech. sedimentation method

Origin: Baker & Adams Chem. Co.(1934)

Phase: in KBr